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(54) Title: COMPOSITIONS OF POLYSILOXANES AND QUATERNIZED FATTY ACID AMIDES

(57) Abstract: A pleasantly soft hand of textile fabrics can be achieved by treating them with aqueous solutions or dispersions which comprise polysiloxanes and quaternized fatty acid amides. The polysiloxanes can have polyalkylene groups and (quaternized) amino groups. The solutions or dispersions have excellent stability.

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Compositions of polysiloxanes and quaternized fatty acid amides

Description

The invention relates to aqueous solutions or dispersions which comprise polydiorganosiloxanes and quaternized fatty acid amides. It further relates to the use of such solutions or dispersions for the treatment of fiber materials, in particular of fabrics.

From a large number of documents it is known to treat fabrics, such as wovens or knits with aqueous dispersions of polydiorganosiloxanes. This imparts water-repellent properties and/or pleasantly soft hand to the textiles.
Polysiloxanes which contain quaternized nitrogen atoms in side chains have also already been used for the purpose of textile finishing. This is evident inter alia from DE-A 196 52 524. The co-use of (quaternized) fatty acid amides is not mentioned in this specification.
Quaternized fatty acid amides are known per se, e.g. from US 4 977 204. This describes compositions which comprise quaternized fatty acid alkanolamides and through which the depth of dying of textiles can be increased. Compositions which also comprise silicones in addition to the quaternized fatty acid alkanolamides are not mentioned.

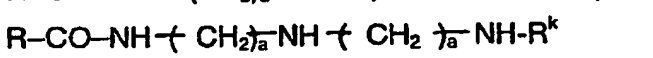
It has been found that the simultaneous use of both polysiloxanes and also of fatty acid amides affords advantages with regard to the properties of finished textiles compared with finishing with only one of these two components. Aqueous dispersions which comprise polysiloxanes and nonquaternized fatty acid alkanolamides have therefore already been used for the treatment of fabrics. This is described in EP-A 578 144 and in US 3 956 350.
This combination, known from the prior art, of polysiloxanes with nonquaternized fatty acid alkanolamides offers the advantage that compositions can be obtained thereby which have the advantages of both classes of product. Thus, it is possible to provide textiles with very pleasantly soft hand and a fluffy character if they are treated with aqueous dispersions of this product combination. Moreover, such aqueous dispersions have the advantage that they only have a low tendency toward undesired foaming.
Aqueous dispersions which comprise polysiloxanes and nonquaternized fatty acid amides, however, also have disadvantages. Thus, for example, their storage and/or thermal stability is

not always optimal. This is true particularly when the polysiloxanes contain quaternized positively charged nitrogen atoms. Said disadvantage thus becomes more evident as the nitrogen content in the polysiloxane increases or as the weight fraction of nitrogen-containing polysiloxane in the dispersion increases. On the other hand, however, the use of nitrogen-containing polysiloxanes is in many cases desired due to their positive properties. These positive properties consist, firstly, primarily in imparting a pleasantly soft hand to finished textiles. On the other hand, polysiloxanes which contain quaternized nitrogen atoms are preferred if the finished fabrics are to have marked hydrophilicity.
A further disadvantage of aqueous dispersions which comprise polysiloxanes and nonquaternized fatty acid amides is that the hydrophilicity of textiles finished with these dispersions is inadequate for many fields of use.

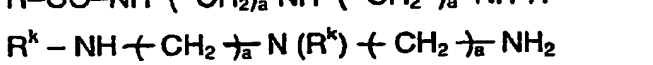
The object of the present invention was to provide compositions which are highly suitable for treating fabrics, which have the advantages of known aqueous polysiloxane/fatty acid amide compositions, but which are free from the abovementioned disadvantages.

The object is achieved by a composition in the form of an aqueous solution or an aqueous dispersion which comprises the following components:
A) a polydiorganosiloxane
B) a quaternized fatty acid amide derived from a fatty acid amide of the formula (Ia) or of the formula (Ib) or of the formula (Ic) by quaternization of one or more nitrogen atoms,

$$R\text{–}CO\text{-}NR^1\text{-}(CH_2)_a\text{-}NR^1\text{-}(CHR^2\text{-}CHR^3\text{-}O)_b\text{-}H \qquad (Ia)$$



$$R\text{–}CO\text{–}NH\text{-}(CH_2)_a\text{-}NH\text{-}(CH_2)_a\text{-}NH\text{-}R^k \qquad (Ib)$$



$$R^k\text{–}NH\text{-}(CH_2)_a\text{-}N(R^k)\text{-}(CH_2)_a\text{-}NH_2 \qquad (Ic)$$

or a mixture of such quaternized fatty acid amides,
where the anions assigned to the quaternized nitrogen atoms are chosen from chloride anions, methylsulfate anions, benzenesulfonate anions or toluenesulfonate anions, preferably toluenesulfonate anions or benzenesulfonate anions,
where

R is a linear or branched alkyl radical having 6 to 24 carbon atoms,

all of the radicals R^k, independently of one another, are H or -CO-R, but where in formula (Ic) at least one of the radicals R^k is -CO-R,

all of the radicals R^1, independently of one another, are hydrogen, a linear or branched alkyl radical having 1 to 8 carbon atoms or are a radical $\{CHR^2\text{-}CHR^3\text{-}O)_b\text{-}H$,

in each unit $\{CHR^2\text{-}CHR^3\text{-}O\}$ one of the radicals R^2 and R^3 is hydrogen and the other is hydrogen or CH_3,

a is a number from 2 to 6 and
b is a number from 1 to 24.

The invention accordingly provides aqueous solutions or dispersions which, in addition to water, comprise at least one each of the abovementioned components A) and B), and also the use of these solutions or dispersions for the treatment of fiber materials.

The composition according to the invention which comprises component A, component B and optionally further components may be in the form of an aqueous solution, namely when this mixture is water-soluble (this is possible, for example, when component A) contains polar groups such as polyoxyalkylene groups or groups with quaternized nitrogen atoms). In the normal case, however, it is in the form of an aqueous dispersion, e.g. an emulsion, and in this case additionally comprises, as component C), a dispersant or a mixture of dispersants.

Compositions according to the invention are highly suitable for the treatment of fiber materials, in particular of fabrics, such as wovens or knits, and have the following advantages:

1. They have excellent stability, even after prolonged storage and even if component A) (polysiloxane) contains quaternized nitrogen atoms in the form of positively charged ammonium groups. This stability is also present when the concentration of such a component A) in the composition is so high that, in combination with exclusively nonquaternized fatty acid amides, it would lead to instability of the solution or dispersion.

2. They exhibit no or only a slight undesired tendency toward foaming. This plays an important role during the treatment of fiber materials in the course of textile finishing, where a tendency toward foaming is undesired.

3. Due to the content of polar, i.e. ionic, components, they have a hydrophilicity which is adequate for normal requirements and which thus also can be transferred to finished textiles. A further increase in the hydrophilicity can be achieved by preferred

embodiments, according to which the polydiorganosiloxane (component A) also contains polar groups, such as, for example, polyoxyalkylene groups and/or groups with quaternized nitrogen atoms.

For some intended uses, on the other hand, polysiloxanes are required which do not have reactive side chains, but hydroxyl groups at the ends of the chains. Such polysiloxanes are thus, for example, linear nitrogen-free polymers which have units of the formula

$HO(CH_3)_2Si-O-$

at both chain ends, and only units of the formula

$-Si(CH_3)_2-O-$

within the chain. In this case, hydrophilicity cannot be transferred to the polysiloxanes via nitrogen-containing radicals.

If such polysiloxanes are combined with quaternized fatty acid amides, then compositions according to the invention are obtained which impart the hydrophilicity which is often required and which in this case could not be achieved through the polysiloxane on its own to textiles.

4. In cases where component A) should likewise contain quaternized nitrogen atoms, an economical method of preparing compositions according to the invention consists in carrying out a quaternization reaction in an aqueous dispersion. This dispersion comprises nonquaternized amino-functional polydiorganosiloxane and nonquaternized fatty acid amide which contains, apart from the amide nitrogen, also at least one quaternizable amino group. By adding a quaternizing agent, e.g. an alkylating agent, the quaternization of the polysiloxane and of the fatty acid amide can be achieved simultaneously in a single operation.

5. Textiles finished with compositions according to the invention have a pleasantly soft hand which is not too dry.

Compositions according to the invention are aqueous solutions or dispersions. These must comprise a quaternized fatty acid amide (component B). This component B) is a product derived from a fatty acid alkanolamide of the formula (Ia) or from a fatty acid amide of the formula (Ib) or of the formula (Ic)

$$R\text{–}CO - NR^1 \text{–}(CH_2)_a\text{–} NR^1 \text{–}(CHR^2 - CHR^3 - O)_b\text{–}H \qquad \text{(Ia)}$$

$$R\text{–}CO\text{–}NH \text{–}(CH_2)_a\text{–}NH \text{–}(CH_2)_a\text{–}NH\text{-}R^k \qquad \text{(Ib)}$$

$$R^k - NH \text{–}(CH_2)_a\text{–} N(R^k) \text{–}(CH_2)_a\text{–}NH_2 \qquad \text{(Ic)}$$

by quaternization of one or more nitrogen atoms, such that this nitrogen atom (or these nitrogen atoms) has four chemical bonds and has a positive electric charge. Consequently, a method of preparing a component B) consists in reacting a fatty acid amide of the formula (Ia), (Ib) or (Ic) or a mixture of such amides of the formulae (Ia), (Ib) or (Ic) with a quaternizing agent, e.g. with an alkylating agent. Component B) may be a uniform chemical compound. However, it is normally a mixture of compounds whose individual representatives differ, for example, by virtue of the chain length of the radical R. In addition, a mixture of quaternized compounds may be present which comprises both quaternized compounds derived from formula (Ia), and also quaternized compounds derived from formula (Ib) and/or (Ic).

Said reaction (quaternization) can be carried out by generally known methods of organic chemistry.

Fatty acid amides of the formulae (Ia), (Ib) and (Ic) are available commercially, in some cases in the form of their salts. One example is the product BELFASIN 2597 from Cognis, DE.

Particularly suitable as component B) of compositions according to the invention are products or product mixtures which can be obtained by quaternization of fatty acid alkanolamides of the formula (Ia), in particular of compounds of the formula (IX)

$R\text{-}CO\text{-}NH\text{-}CH_2CH_2\text{-}NH\text{-}CH_2CH_2OH$ (IX).

R here has the meaning given in claim 1. Compounds of the formula (IX) can be obtained by the reaction of

RCOOH with $H_2NCH_2CH_2NHCH_2CH_2OH$

or with ethylenediamine and subsequent reaction with ethylene oxide.

In the formulae (Ia), (Ib) and (Ic), from which component B) is derived by quaternization of at least one nitrogen atom, all of the radicals R^1, independently of one another, are hydrogen, a linear or branched alkyl radical having 1 to 8 carbon atoms or a radical of the formula $-(CHR^2\text{-}CHR^3\text{-}O\text{-})_bH$.

One of the radicals R^2 and R^3 here is hydrogen, and the other is likewise hydrogen or is CH_3. b is a number from 1 to 24, b preferably has the value 1 in formulae (Ia). In the formulae (Ib) and (Ic), all of the radicals R^k present are, independently of one another, H or are -CO-R. In formula (Ic), however, at least one of the radicals R^k must be -CO-R. In the formulae (Ia) and (Ib), the radicals R are in each case a linear or branched alkyl radical) having 6 to 24 carbon atoms.

As formula (Ia) shows, compounds of the formula (Ia) must always contain at least one group $-(CHR^2\text{-}CHR^3\text{-}O\text{-})_bH$, irrespective of whether one or more of the radicals R^1 additionally stand for this group. The statements made above with regard to R^2, R^3 and b are also valid for this group which must always be present if component B) is a quaternized fatty acid alkanolamide derived from a compound of the formula (Ia).

In the formulae (Ia) and (Ib), a is a number from 2 to 6. a preferably has the value 2.
The radical R in the formulae (Ia) and (Ib) is a linear or branched alkyl radical having 6 to 24 carbon atoms, preferably a saturated, unbranched alkyl radical having 8 to 18 carbon atoms. The same statement is valid for the radicals R in all of those radicals R^k in the formulae (Ib) and (Ic) which stand for -CO-R.
Even if compositions according to the invention are to comprise a component B) derived from only one of the formulae (Ia), (Ib) or (Ic), for the quaternization reaction, preference is given, for cost reasons, not to using a chemical uniform compound of the formula (Ia), (Ib) or (Ic), but a mixture of compounds which conform to one of these formulae and whose individual representatives differ in the chain length of the radical R. One example of this is a mixture which is formed by reacting hydrogenated tallow fatty acids with H_2N-CH_2-CH_2-NH-CH_2CH_2OH.
For the purpose of quaternization, the compounds of the formulae (Ia) to (Ic) can either be used as such or in the form of salts, e.g. those which are formed by reacting a compound of the formula (Ia), (Ib) or (Ic) with acetic acid. Where appropriate, when such salts are used, the pH of the reaction mixture must be optimized.

Compounds of the formula (Ia), (Ib) and (Ic) are available commercially.
In addition, compounds of these formulae can be prepared by known methods by reacting the corresponding fatty acid RCOOH or a mixture of such fatty acids with the corresponding amines. One example of the preparation of compounds of the formulae (Ib) and (Ic) is the reaction of technical-grade stearic acid (i.e. a mixture of fatty acids whose individual compounds differ in the chain length of the alkyl radical) with diethylenetriamine ((N-2-aminoethyl)ethylenediamine).

In the preparation of the amides of the formulae (Ia), (Ib) and (Ic), esters may also arise as byproducts (e.g. from fatty acid and H_2N-CH_2CH_2-NH-CH_2CH_2-$NHCH_2CH_2OH$ by reaction of the carboxyl group with the hydroxyl group). In addition, cyclic compounds may form, e.g. imidazoline derivatives by intramolecular reaction, in which the carbonyl group of the amide of the formula (Ia) reacts with a nitrogen atom of this amide, and water is subsequently cleaved off. During the subsequent quaternization of the amide, the corresponding imidazoline is also partially or completely quaternized.
Said byproducts originating from the amide synthesis do not have to be separated off. Compositions according to the invention can also be used for the treatment of textiles if they comprise these byproducts. In some cases, it has even proved to be advantageous if said quaternized imidazoline derivatives were additionally present in compositions according to the invention. The stability of aqueous dispersions of compositions according to the invention was further improved thereby.

The quaternization of the compounds of the formula (Ia), (Ib) or (Ic), which leads to component B) of compositions according to the invention, is carried out such that, in component B), the anions assigned to the quaternized nitrogen atoms are chosen from chloride anions, methylsulfate anions, benzenesulfonate anions and toluenesulfonate anions. Methylsulfate anions, benzenesulfonate anions and toluenesulfonate anions are preferred; the toluenesulfonate anions may be chemically uniform anions or isomeric mixtures.
As early as this it may be mentioned that also in cases where polysiloxanes with quaternized nitrogen atoms are used as component A), the corresponding anions are preferably likewise chosen from said classes of anions, in which case the anions here are also preferably methylsulfate anions, benzenesulfonate anions or toluenesulfonate anions.
In view of these statements about the anions, suitable compounds for the quaternization reaction are, inter alia, the following:
Alkyl chlorides, dimethyl sulfate, benzenesulfonic alkyl esters, toluenesulfonic alkyl esters.
For the purposes of the invention, quaternized fatty acid amides are to be understood as meaning only compounds which contain at least one nitrogen atom with a positive electric charge and which has 4 bonds, each to one carbon atom.

If component (B) is prepared by quaternization of compounds of the formula (Ia), (Ib) and/or (Ic) in which one or two hydrogen atoms are also bonded to the nitrogen atom which is to be quaternized, then it must be ensured that sufficient quaternizing agent is used so that no hydrogen atom is any longer bonded to this nitrogen atom after the quaternization, but all hydrogen atoms bonded to N have been substituted by the corresponding organic radical so that 4 carbon atoms are directly bonded to at least one nitrogen atom.
In addition, compositions according to the invention can also additionally comprise further quaternized fatty acid amides. One example is
$R\text{-}CO\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2CH_2\text{-}NH\text{-}CH_2CH_2NH\text{-}CH_2CH_2\text{-}NH_2$ in the form of quaternized derivatives. R here has the meaning given above and in claim 1.

In addition to the above-described component B) (quaternized fatty acid amide), compositions according to the invention must also comprise at least one component A). Component A) is a polydiorganosiloxane.
Polydiorganosiloxanes (silicones) are known polymers, e.g. those of the general formula $R'_3Si\text{-}O\text{-}(SiR'_2O\text{-})_tSiR'_3$.

In these polyorganosiloxanes which can be used as component A) of compositions according to the invention, t is normally a number in the range from 10 to 2000. All of the radicals R',

independently of one another, are organic radicals, and in some cases one or more of the radicals R' may also be -OH or -OR^4, where R^4 is an alkyl radical having 1 to 4 carbon atoms or is the phenyl radical.

However, more than one radical -OH or -OR^4 is not bonded to any silicon atom. Preferably, OH or OR^4 groups, if present at all, are located exclusively on one of the two chain ends of the polysiloxanes.

Normally, component A) is not a chemically uniform compound, but a mixture of compounds as is customary for polymers. The individual representatives of this mixture differ, for example, by the chain length, i.e. by the value of t. However, analogously to the case of component B), it is also possible to use, as component A), a mixture of polysiloxanes whose individual representatives differ not only in the chain length, but, for example, in the nature of the individual radicals R'. Thus, as component A), it is possible, for example, to use a mixture of 2 polysiloxanes, one of which contains units of the formula (III) described in more detail below, in which X is a radical of the formula (IV), and the other of which contains units of the formula (III) in which X is a radical of the formula (V).

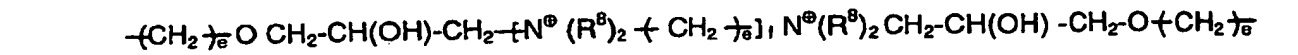
As component A), it is also possible to use polysiloxanes of the abovementioned general formula

$R'_3Si\text{-}O\text{-}(SiR'_2O\text{-})_tSiR'_3$

in which, within the polydiorganosiloxane chain, units are also additionally present which do not have the structure

$-SiR'_2O-$

but are units of the formula (M)



(M)

In formula (M),

e is a number from 2 to 6

f is the number 1 or 2

R^8 is an alkyl radical having 1 to 18 carbon atoms, preferably CH_3.

A particularly advantageous and therefore preferred embodiment of compositions according to the invention is characterized in that component A) is a polydiorganosiloxane whose two end-groups are formed by units of the formula

$R^5R^4_2Si\text{-}O-$

and which contains, in the polysiloxane chain, units of the formula (II)

$-Si(R^4)_2-O-$ (II)

and units of the formula (III)

$-Si(R^4)(X)-O-$ (III)

where

R^4 is an alkyl radical having 1 to 4 carbon atoms or the phenyl radical and R^5 is R^4 or is X or is OR^4 or is OH or is a radical of the formula (W),

$$R^9\text{-}\overset{\oplus}{N}\text{-}(R^{10})_2\text{-}(CH_2)_g\text{-}[\overset{\oplus}{N}(R^{10})_2CH_2]_t\text{-}CH(OH)\text{-}CH_2\text{-}O\text{-}(CH_2)_g \quad (W)$$

in which
R^9 is hydrogen or a linear or branched alkyl radical having 1 to 12 carbon atoms,
R^{10} is an alkyl radical having 1 to 18 carbon atoms, preferably CH_3,
g is a number from 2 to 6,
t has the value 0 or 1,
all of the radicals X, independently of one another, are a radical of the formula (IV)

$-R^6\text{-}(CHR^2\text{-}CHR^3\text{-}O)_b\text{-}R^7$ (IV)

or of the formula (V)

$-R^6\text{-}[NR^1\text{-}R^6]_c\text{-}NR^1_2$ (V)

where, R^1, R^2, R^3 and b have the meanings given in claim 1 and c has the value 0, 1 or 2,
all of the radicals R^6, independently of one another, are in each case a branched or unbranched divalent alkylene radical having 2 to 6 carbon atoms and
R^7 is H or CH_3,
or where one or more of the radicals X are a radical derived from a radical of the formula (V) such that one or more of the nitrogen atoms present are in quaternized form.

Preferably, polysiloxanes which are used as component A) contain, within the polymer chain, no units other than those of the formulae (II) and (III), and no end-groups other than $R^5R_2^4Si-O-$.

The end-groups of these preferred polysiloxanes are formed by units of the formula $R^5R_2^4Si$-O-, where R^5 and R^4 have the meanings given above. Preferred end-groups are

$HO(CH_3)_2Si$-O-

and

$(CH_3)_3Si$-O-

Further suitable end-groups are $(CH_3O)(CH_3)_2Si$-O- and $(C_2H_5O)(CH_3)_2Si$-O-.

Within the polysiloxane chain of these polysiloxanes preferred as component A), units of the formula (II)

$-Si(R^4)_2-O-$ (II)

and of the formula (III)

$-Si(R^4)(X)-O-$ (III)

are present. The radicals R^4 here are an alkyl radical having 1 to 4 carbon atoms or the phenyl radical, and preferably 80 to 100% of the radicals R^4 present are methyl groups. In addition, in these polysiloxanes which are particularly highly suitable as component A), all of the radicals X present are, independently of one another, a radical of the formula (IV)

$$-R^6-(CHR^2-CHR^3-O)_b-R^7 \quad (IV)$$

or of the formula (V)

$$-R^6-[NR^1-R^6]_c-NR^1_2 \quad (V)$$

One or more of the radicals X can also in each case be a radical derived from a radical of the formula (V) such that one or more of the nitrogen atoms present are in quaternized form. If radicals X are present which contain one or more quaternized nitrogen atoms, then the corresponding anions are preferably chosen from the same anions as described above and in claim 1. The distribution of the individual units of the formulae (II) and (III) over the polysiloxane chain may be arbitrary.

In all of the radicals of the formula (IV), at least one the radicals R^2 and R^3 is hydrogen. The other can be a methyl group, but preferably in 50 to 100% of all units of the formula (IV), both R^2 and also R^3 are hydrogen. In this case, the polyorganosiloxanes used as component A) are polyoxyethylene units, through the number of which it is possible to control the hydrophilicity of compositions according to the invention and of textiles treated therewith in a targeted manner. In formula (IV), b has a value from 1 to 24, preferably from 6 to 24, R^6 is a branched or unbranched divalent alkylene radical having 2 to 6 carbon atoms, and R^7 is H or CH_3.

In formula (V), R^6 and R^1 have the meanings already given above. c has the value 0, 1 or 2. Thus, polysiloxanes suitable as component A) have one or more side chains in which, in each case, 1, 2 or 3 nitrogen atoms are present. It is particularly preferred if, in formula (V), R^6 contains 2 or 3 carbon atoms and all of the radicals R^1 are an alkyl group having 1 to 4 carbon atoms, in particular a methyl group. These statements also apply if radicals X are present which contain quaternized nitrogen atoms, i.e. are derived from a radical (V) by quaternization thereof. Thus, no N-H bonds are preferably present in radicals (V) or quaternized derivatives thereof.

A particularly suitable component A) of compositions according to the invention is a polysiloxane whose end-groups are formed by units of the formula

$(CH_3)_3Si$-O-

and which has units of the formula

-$Si(CH_3)_2$-O-

and of the formula (VI)

-$Si(CH_3)(X^1)$-O- (VI),

in the polysiloxane chain, where all of the radicals X^1, independently of one another, are a radical of the formula (VII)

$$-(CH_2)_a-(CHR^2-CHR^3-O)_d-H \qquad (VII),$$

where d is a number from 6 to 24 and R^2 and R^3 have the meanings given in claim 1,

or is a radical of the formula (VIII)

$$-(CH_2)_a-NR^1-(CH_2)_a]_c-NR^1_2 \qquad (VIII),$$

where a is a number from 2 to 6 and c has the value 0, 1 or 2,

or is a radical derived from a radical of the formula (VIII) such that one or more nitrogen atoms are present in quaternized form.

In a further preferred embodiment of compositions according to the invention, the polydiorganosiloxane comprises both side chains with polyoxyethylene units on the one hand and side chains with amino groups or quaternized nitrogen atoms on the other hand. This embodiment is characterized in that component A) contains both radicals of the formula (VI) in which X^1 is a radical of the formula (VII), and also radicals of the formula (VI) in which X^1 is a radical of the formula (VIII), or is a radical of the formula (VIII) in with one or more nitrogen atoms are present in quaternized form.

Such polydiorganosiloxanes and their preparation are described in US 5 612 409. The preparation can be carried out by reacting linear or cyclic poly- or oligodialkylsiloxanes with bisalkoxyalkylsilanes which additionally comprise a radical with an amino group, and with trisiloxanes of the formula $(CH_3)_3Si$-O-$Si(CH_3)(X^1)$-O-$Si(CH_3)_3$, where X^1 is a radical of the

formula (VII); such trisiloxanes are available from Goldschmidt, DE. Said bisalkoxyalkylsilanes are monomeric compounds of the general formula $(RO)_2Si(R)(R'')$, where R is an alkyl radical and R" is a radical which comprises one or more amino groups.

In analogous manner to the details in said US specification, it is also possible to prepare polysiloxanes which contain only radicals with amino groups, but no polyoxyethylene units, or polyoxyethylene-group-containing polysiloxanes which do not contain amino groups. For this, in the synthesis, either only the abovementioned bisalkoxyalkylsilane or only said trisiloxane is used. The polysiloxanes obtained in this way are also suitable as component A) of compositions according to the invention. Polysiloxanes which have amino groups in side chains can also be prepared by known methods, e.g. by adding corresponding allylamines onto a polysiloxane which contains Si-H bonds. In addition, amino functional polysiloxanes which are suitable as component A) are customary commercially available products, e.g. from Dow Corning and Wacker.

Polydiorganosiloxanes which contain both polyoxyethylene groups and also amino groups are therefore particularly preferred because they impart a pleasantly soft hand and a hydrophilicity which can be controlled in a targeted manner to the textiles finished therewith.

In polysiloxanes which are suitable as component A), amino-group-containing radicals other than those mentioned above may also be present. Examples thereof are the amino-group-containing radicals bonded to a silicon atom mentioned in US 5 310 783, in particular radicals of the formulae (II), (III), (IV) (column 4, lines 50 to 60 of this US specification), and also the nitrogen-containing radicals mentioned in claim 4 of EP-A 1 076 078.

It has been found that for many intended uses it is advantageous if polysiloxanes which contain amino groups and are to be used as component A) of compositions according to the invention contain only tertiary, i.e. no primary or secondary, amino groups. This is true particularly if the amino-functional polysiloxanes as such are not to form the component A), but polysiloxanes are derived from the amino-functional ones such that one or more nitrogen atoms are in quaternized form. This can be carried out by reacting the parent amino-functional polysiloxanes with a quaternizing agent. The quaternizing agent here may be an alkyl chloride, dimethyl sulfate or an alkyl ester of benzenesulfonic acid or toluenesulfonic acid. It is particularly advantageous if the quaternization of the amino-functional polysiloxane is carried out simultaneously in a single operation to the quaternization of the fatty acid amide, i.e. to the preparation of component B). This quaternization can be carried out by known methods in an aqueous dispersion or solution which comprises amino-functional polysiloxane and the nonquaternized fatty acid amide. However, even when the quaternization of fatty acid amide and polysiloxane is not carried out simultaneously, all of the anions which are assigned to the quaternized nitrogen atoms of component B) in compositions according to the invention are chosen from chloride anions,

methylsulfate anions, benzenesulfonate anions and toluenesulfonate anions. The anions which are assigned to quaternized nitrogen atoms in component A) are likewise chosen from the anions mentioned here.

Component A) may also be a mixture of different polysiloxanes, although this mixture preferably consists of only polysiloxanes which contain no units other than those of the formulae (II) and/or (III)

$-Si(R^4)_2-O-$ (II)

$-Si(R^4)(X)-O-$ (III)

in the chain. These formulae have been explained above. Preferably, all of the polysiloxanes which are used as component A) contain units of the formula (II). In addition, it is advantageous if, in addition to units of the formula (II), units of the formula (III) are also present. The distribution of the individual units of the formulae (II) and (III) over the polysiloxane chain may be arbitrary.

It is favorable if the ratio of the number of units of the formula (II) to the number of units of the formula (III) is greater than 1; this ratio is preferably 10:1 to 200:1.

If the mixture of components A) and B) present in compositions according to the invention is not soluble in water or self-dispersing, then compositions according to the invention are in the form of aqueous dispersions and, in addition to components A) and B), also additionally comprise a component C).

Component C) is a dispersant or a mixture of dispersants. Suitable dispersants are the known surface-active products, as are known to the person skilled in the art, for example for the preparation of silicone emulsions. Compositions according to the invention which are in the form of aqueous dispersions preferably comprise, as dispersants, only nonionic and/or cationic surface-active products, but no anionic ones. Of the nonionic surfactants, particular preference is given to ethoxylated fatty alcohols or ethoxylated fatty acids. Other suitable dispersants are known surfactants, such as alkyl polyglycosides and ethoxylated branched diols having 4 to 8 carbon atoms in the diol component. Of the cationic surfactants, preference is given to quaternary ammonium salts with at least one long-chain organic radical bonded to nitrogen, e.g. an alkyl or alkenyl radical having 8 to 20 carbon atoms.

Compositions according to the invention preferably comprise

20 to 95% by weight of water

and

3 to 70% by weight of component A), preferably 5 to 50% by weight

2 to 30% by weight of component B), preferably 5 to 25% by weight

and
0 to 30% by weight of component C).

The sum of the amounts of water and of components A), B) and C) which are present in an individual case must not be 100% by weight of the composition according to the invention. Rather, the compositions can comprise further products, as are customary and known for textile finishing. These include, for example, cellulose crosslinkers, flame retardants and polymers which contain fluorine.

The compositions according to the invention can normally be prepared by generally known methods, such as, for example, simple mixing of component A), component B), water and optionally further components, and mechanical homogenization at room temperature. In individual cases it is possible that it is necessary to work at elevated temperature or that it is necessary to observe a certain order of mixing or dispersing. Thus, for example, a preprepared aqueous dispersion of a polydioganosiloxane can be combined with an aqueous solution or dispersion of a fatty acid amide. In this connection, it is possible that the fatty acid amide in the second dispersion is already in quaternized form, i.e. as component B). However, it may also be in nonquaternized form in the second dispersion, meaning that the quaternization is only carried out after the two dispersions have been combined. This latter procedure is preferred if quaternized nitrogen atoms are also to be present in component A) (polysiloxane) in finished compositions according to the invention. In this case, the quaternization of the polysiloxane and of the fatty acid amide can be comfortably achieved in a single operation.
However, to undertake quaternization of the fatty acid amide only in a mixture which already comprises polydiorganosiloxane is also possible if a nitrogen-free polysiloxane is to be used as component A), e.g. an α,ω-dihydroxypolydimethylsiloxane. In addition, in certain cases, it is possible and often even advantageous to carry out the preparation of component A) in the presence of a fatty acid amide, in which case it is possible for the latter either to already be in quaternized form as component B) or to be quaternized at a later time. One example is the emulsion polymerization, carried out in aqueous systems, of a polysiloxane precursor for the purposes of preparing an α,ω-dihydroxypolydimethylsiloxane. It has proven favorable to carry out this emulsion polymerization in the presence of a fatty acid amide which either falls under one of the formulae (Ia), (b) or (Ic) given in claim 1 and is quaternized after the emulsion polymerization, giving component B), or which is already in the form of component B). The mixture in which the emulsion polymerization is carried out normally already comprises a suitable dispersant or a mixture of dispersants, meaning that, after the polymerization, a stable composition according to the invention is obtained.

Compositions according to the invention are highly suitable for the treatment of fiber materials, to which a pleasantly soft hand can be thereby imparted. The fiber materials are preferably fabrics in the form of wovens or knits. They can consist of a very wide variety of materials, such as, for example, cellulose fibers, regenerated cellulose fibers, synthetic fibers or mixtures of these types of fiber. The compositions according to the invention are applied to fabrics preferably in the course of textile finishing, i.e. before manufacturing and after dyeing. Application can be carried out by means of a known padding process, where the concentration of the padding liquor may be within the customary limits known to the person skilled in the art. For this, approximately 20 to 150 g of composition according to the invention are normally used per liter of padding liquor. Further processing of the finished textiles can likewise be carried out by known methods. In this way, it is possible to prepare, inter alia, articles of clothing.

The invention is illustrated below by working examples.

Example 1 (noninventive comparative example)

According to this example, an aqueous dispersion was prepared which comprised a polydiorganosiloxane and a fatty acid alkanolamide. The difference between this dispersion and a composition according to the invention consisted in the fact that the fatty acid alkanolamide was not in quaternized form, i.e. no component B) was present.

a) Preparation of an aqueous dispersion of an amino-functional polysiloxane:

48 g of a linear polydimethylsiloxane (silicone oil AK 2000, Wacker)
0.83 g of $(C_2H_5O)_2Si(CH_3)CH_2CH_2CH_2NH_2$
0.13 g of 45% strength aqueous potassium hydroxide solution
5.5 g of $(CH_3)_3Si\text{-}O\text{-}Si(CH_3)(X)\text{-}O\text{-}Si(CH_3)_3$ (trisiloxane from Goldschmidt, Essen, DE)
X = a monovalent radical which contains polyoxyethylene groups and polyoxypropylene groups and
0.28 g of water

were mixed together and heated at about 115°C for 3 hours. The mixture was then cooled to 90°C,
34 g of water
6.4 g of a mixture of ethoxylated alcohols
and 2.4 g of dipropylene glycol were added. The mixture was cooled to 50°C, then 2 g of 60% strength aqueous acetic acid solution were added and the mixture was mechanically

homogenized, giving a stable silicone microemulsion. The silicone had side chains with amino groups and side chains with polyoxyalkylene groups.

b) Preparation of an aqueous dispersion of amino-functional polysiloxane and fatty acid alkanolamide

In a reaction vessel,
5 g of 60% strength aqueous acetic acid solution
498 g of water heated to 60°C
50 g of a fatty acid alkanolamide in salt form (BELFASIN 2597 conc PI, Cognis, DE), this is a salt of a mixture of compounds of the formula (Ia) according to claim 1 and acetic acid and
20 g of quaternary ammonium salt (cation is an ammonium ion with a methyl group a $-CH_2CH_2OH$ group and 2 longer-chain groups on the N atom; anion = CH_3SO_4)
were mixed together and
kept at 80°C with stirring for 30 minutes.
The mixture was then cooled to 45°C and 197 g of water were firstly added, followed by 230 g of the silicone microemulsion obtained as above under a). Mechanical homogenization for 30 minutes gave a low-viscosity, pale-yellow colored emulsion with a pH of about 3.8 at 20°C. This aqueous emulsion, which contained a nonquaternized amino-functional polysiloxane and a nonquaternized fatty acid alkanolamide, is referred to below as "comparison dispersion 1". The comparison dispersion 1 was a liquid, opal dispersion which was still stable even after storage for 10 days.

Example 2 (noninventive comparative example)

Although comparison dispersion 1 prepared as in example 1 imparted a certain level of hydrophilic properties to the textiles finished therewith, this level was not regarded as adequate for all intended uses. For this reason, according to this example 2, an aqueous dispersion was prepared (= "comparison dispersion 2") by combining 30 parts by weight of comparison dispersion 1 and 70 parts by weight of an aqueous dispersion of a polysiloxane with quaternized nitrogen atoms. To prepare this polysiloxane, which contained radicals with quaternized nitrogen atoms in side chains, an amino-functional polysiloxane was firstly prepared by means of a known equilibrium reaction from

90 g of octamethylcyclotetrasiloxane
5.2 g of $(CH_3O)_2Si(CH_3)CH_2CH_2CH_2NHCH_2CH_2NH_2$

2 g of the trisiloxane given in example 1 from Goldschmidt
1.5 g of water
and
0.22 g of 45% strength aqueous KOH solution.
15 g of this amino-functional polysiloxane was dispersed in 70 g of water using 10 g of a mixture of ethoxylated isotridecyl alcohols. The mixture was then quaternized using 3.6 g of methyl p-toluenesulfonate.
The comparison dispersion 2 comprised no quaternized fatty acid amide and, after storage for 10 days at room temperature, exhibited crumbly, sandy deposits, i.e. was insufficiently stable for suitability for textile treatment. On the other hand, textiles which had been treated with comparison dispersion 2 had improved hydrophilicity compared with textiles which were treated with comparison dispersion 1.

Example 3 (according to the invention)

In order to retain the hydrophilic properties compared with those which can be achieved with comparison dispersion 2 and to improve the stability of the dispersion, a dispersion according to the invention (= "dispersion 3") was prepared which, in contrast to comparison dispersion 2, comprised a quaternized fatty acid alkanolamide.
Dispersion 3 was prepared by combining 70 parts by weight of the aqueous dispersion of a polysiloxane with quaternized nitrogen atoms (as described in example 2), with 30 parts by weight of an aqueous polysiloxane dispersion which comprised a quaternized fatty acid alkanolamide. This dispersion which comprised the quaternized fatty acid alkanolamide consisted of 35% by weight of the polysiloxane dispersion which was obtained as in step a) of example 1 and 65% by weight of a mixture which comprised quaternized fatty acid alkanolamide. This mixture can be prepared by reacting 40 g of fatty acid alkanolamide (BELFASIN as described in example 1) with 3.5 g of methyl p-toluenesulfonate in the presence of 450 g of water and 8 g of propylene glycol at room temperature and subsequent heating to 60°C.
Using dispersion 3 according to the invention, a pleasantly soft hand and excellent hydrophilicity can be imparted to textiles. This hydrophilicity is higher than in the case of the treatment of the textiles with comparison dispersion 1. The stability of dispersion 3 is significantly better than that of comparison dispersion 2. Even after storage for 10 day at room temperature, dispersion 3 was still homogeneous.

In example 3, a dispersion of a polysiloxane with quaternized nitrogen atoms was combined with a polysiloxane dispersion, prepared separately therefrom, which comprised a quaternized fatty acid alkanolamide in order to obtain dispersion 3 according to the invention.

Example 4 (according to the invention)

In a further experiment, prior to carrying out the quaternization, the aqueous dispersion of an amino-functional (nonquaternized) polysiloxane was combined with an aqueous dispersion which comprised a (nonquaternized) fatty acid alkanolamide. The quaternization was thus carried out directly on a mixture which comprised nonquaternized polysiloxane and nonquaternized fatty acid alkanolamide. Following the simultaneous quaternization of fatty acid alkanolamide and amino-functional polysiloxane, an aqueous dispersion of an amino-functional polysiloxane was also added.
The amounts of products used in this example 4 were such that, following simultaneous quaternization of fatty acid alkanolamide and amino-functional polysiloxane and the subsequent addition of further amino-functional polysiloxane, an aqueous dispersion was obtained which had the same chemical composition as dispersion 3 according to the invention. The difference between the dispersions obtained as in examples 3 and 4 was only that in example 3, the polysiloxane and the fatty acid alkanolamide were quaternized separately from one another, whereas in example 4 they were quaternized together.

The dispersion according to the invention obtained in this way likewise had good stability upon storage and had the same properties with regard to hydrophilicity and hand of the finished textiles as dispersion 3.

All of the fabric samples which had been finished with one of the dispersions as in one of examples 1 to 4 by customary methods (padding) had a pleasantly soft hand.

Hydrophilicity and foaming behavior were tested on the dispersions of examples 1 to 3. The results are given in table 1.

Table 1

	Hydrophilicity	Foaming behavior	
		H	D
Example 1 Comparison dispersion 1	40	20	60
Example 2 Comparison dispersion 2	11	20	30
Example 3 Dispersion 3 according to the invention	8	15	20

The hydrophilicity was determined via the wetting of fabric samples by the 3 dispersions. For this purpose, fabric samples of cotton/polyester (50:50) were treated by means of padding with the dispersions and then dried at 110°C for 10 minutes. 1 drop of water was then applied to various places on the surface of the fabric using a dropping device. The time in seconds between application of the drop and the time until the drop was completely absorbed by the fabric was measured; the latter time point is recognizable from the disappearance of the dome initially formed on the fabric by the drop.
This time in seconds is given in table 1 as "hydrophilicity" (average value of the individual results at various places on the surface of the fabric). A lower value accordingly means more rapid wetting and greater hydrophilicity.

To determine the foaming behavior, 0.6 g of each of dispersions 1 to 3 was mixed with 100 ml of water, and these mixtures were each introduced into a 250 ml measuring cylinder. After repeated mechanical circulation of the cylinder sealed with a stopper, the cylinder was positioned vertically and the foam height was immediately read off in ml. In addition, the time (in seconds) after which the foam had completely disintegrated was ascertained. Table 1 gives, under "foaming behavior" in the "H" column the foam height in ml, and in the "D" column, the disintegration time in seconds (in each case average values from 10 determinations).

What is claimed is:

1. A composition in the form of an aqueous solution or an aqueous dispersion which comprises the following components:
A) a polydiorganosiloxane
B) a quaternized fatty acid amide derived from a fatty acid amide of the formula (Ia) or of the formula (Ib) or of the formula (Ic) by quaternization of one or more nitrogen atoms,

$$R\text{–}CO\text{-}NR^1\text{-}(CH_2)_a\text{-}NR^1\text{-}(CHR^2\text{-}CHR^3\text{-}O)_b\text{-}H \quad \text{(Ia)}$$

$$R\text{–}CO\text{–}NH\text{-}(CH_2)_a\text{-}NH\text{-}(CH_2)_a\text{-}NH\text{-}R^k \quad \text{(Ib)}$$

$$R^k\text{–}NH\text{-}(CH_2)_a\text{-}N(R^k)\text{-}(CH_2)_a\text{-}NH_2 \quad \text{(Ic)}$$

or a mixture of such quaternized fatty acid amides,
where the anions assigned to the quaternized nitrogen atoms are chosen from chloride anions, methylsulfate anions, benzenesulfonate anions or toluenesulfonate anions, preferably toluenesulfonate anions or benzenesulfonate anions,

where

R is a linear or branched alkyl radical having 6 to 24 carbon atoms,

all of the radicals R^k, independently of one another, are H or -CO-R, but where in formula (Ic) at least one of the radicals R^k is -CO-R,

all of the radicals R^1, independently of one another, are hydrogen, a linear or branched alkyl radical having 1 to 8 carbon atoms or are a radical $(CHR^2\text{-}CHR^3\text{-}O)_b\text{-}H$,

in each unit $(CHR^2\text{-}CHR^3\text{-}O)$ one of the radicals R^2 and R^3 is hydrogen and the other is hydrogen or CH_3,

a is a number from 2 to 6 and
b is a number from 1 to 24.

2. The composition as claimed in claim 1, characterized in that it is an aqueous dispersion which additionally comprises, as component C), a dispersant or a mixture of dispersants.

3. The composition as claimed in claim 1 or 2, characterized in that component A) is a polydiorganosiloxane, the two end-groups of which are formed by units of the formula
$R^5R^4_2Si$-O-
and which contains, in the polysiloxane chain, units of the formula (II)
$-SiR^4)_2$-O- (II)
and units of the formula (III)
$-Si(R^4)(X)$-O- (III)
where
R^4 is an alkyl radical having 1 to 4 carbon atoms or the phenyl radical and R^5 is R^4 or is OR^4 or is OH,

all of the radicals X, independently of one another, are a radical of the formula (IV)

$-R^6-(CHR^2-CHR^3-O)_b-R^7$ (IV)

or of the formula (V)

$-R^6-[NR^1-R^6]_c-NR^1_2$ (V)

where, R^1, R^2, R^3 and b have the meanings given in claim 1 and c has the value 0, 1 or 2,
all of the radicals R^6, independently of one another, are in each case a branched or unbranched divalent alkylene radical having 2 to 6 carbon atoms and
R^7 is H or CH_3,
or where one or more of the radicals X is a radical derived from a radical of the formula (V) such that one or more of the nitrogen atoms present is in quaternized form.

4. The composition as claimed in claim 3, characterized in that 80 to 100% of all of the radicals R^4 present are methyl radicals.

5. The composition as claimed in claim 3 or 4, characterized in that component A) is a polydiorganosiloxane, the end-groups of which are formed by units of the formula
$(CH_3)_3Si$-O-
and which has, in the polysiloxane chain, units of the formula
$-Si(CH_3)_2$-O-
and of the formula (VI)
$-Si(CH_3(X^1)$-O- (VI),
in which all of the radicals X^1, independently of one another, are a radical of the formula (VII)

$-(CH_2)_a-(CHR^2-CHR^3-O)_d-H$ (VII)

where d is a number from 6 to 24 and R^2 and R^3 have the meanings given in claim 1,

or are a radical of the formula (VIII)

$$-(CH_2)_a-[-NR^1-(CH_2)_a]_c-NR^1_2 \qquad (VIII),$$

where a is a number from 2 to 6 and c has the value 0, 1 or 2,
or are a radical derived from a radical of the formula (VIII) such that one or more nitrogen atoms are in quaternized form.

6. The composition as claimed in claim 5, characterized in that component A) contains both radicals of the formula (VI) in which X^1 is a radical of the formula (VII), and also radicals of the formula (VI) in which X^1 is a radical of the formula (VIII), or is a radical of the formula (VIII) in which one or more nitrogen atoms are in quaternized form.

7. The composition as claimed in one or more of claims 1 to 6, characterized in that component B) is a quaternized fatty acid alkanolamide derived from a fatty acid alkanolamide of the formula (IX)

$$R\text{-}CO\text{-}NH\text{-}CH_2CH_2\text{-}NH\text{-}CH_2CH_2OH \qquad (IX),$$

where R has the meaning given in claim 1, derived such that one nitrogen atom is in quaternized form.

8. The composition as claimed in one or more of claims 1 to 7, characterized in that it comprises
3 to 70% by weight of component A)
2 to 30% by weight of component B)
0 to 30% by weight of component C)
and
20 to 95% by weight of water.

9. The use of a composition as claimed in one or more of claims 1 to 8 for the treatment of fiber materials.

10. The use as claimed in claim 9, characterized in that the fiber materials are fabrics in the form of wovens or knits and that the treatment with the composition takes place within the scope of textile finishing in the non-made up state.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/10416

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L83/04 C08K5/19 D06M15/643

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 183 845 A (PARKINSON JEFF ET AL) 2 February 1993 (1993-02-02) column 8, line 59 - line 67; claim 1	1
A	EP 0 578 144 A (PFERSEE CHEM FAB) 12 January 1994 (1994-01-12) cited in the application page 13, line 15 - line 20; claims 1,6,7	1-10
A	DE 196 52 524 A (RUDOLF GMBH & CO KG CHEM FAB) 18 June 1998 (1998-06-18) cited in the application claim 1	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hoffmann, K

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 02/10416

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5183845	A	02-02-1993	NONE		
EP 0578144	A	12-01-1994	DE	4222483 A1	13-01-1994
			AT	161861 T	15-01-1998
			BR	9302789 A	16-02-1994
			DE	59307912 D1	12-02-1998
			DK	578144 T3	07-09-1998
			EP	0578144 A2	12-01-1994
			ES	2111666 T3	16-03-1998
			JP	7010999 A	13-01-1995
			US	5612409 A	18-03-1997
DE 19652524	A	18-06-1998	DE	19652524 A1	18-06-1998